

Available online at www.sciencedirect.com



Food Chemistry

Food Chemistry 106 (2008) 421-430

www.elsevier.com/locate/foodchem

Analytical, Nutritional and Clinical Methods

# Characterisation of cell wall polysaccharide profiles of apricots (*Prunus armeniaca* L.), peaches (*Prunus persica* L.), and pumpkins (*Cucurbita* sp.) for the evaluation of fruit product authenticity

Christina Kurz, Reinhold Carle, Andreas Schieber\*

Institute of Food Science and Biotechnology, Section Plant Foodstuff Technology, Hohenheim University, August-von-Hartmann-Strasse 3, D-70599 Stuttgart, Germany

Received 7 March 2007; received in revised form 29 May 2007; accepted 29 May 2007

#### Abstract

Cell wall polysaccharides were investigated for their suitability as markers for quality and authenticity control of fruit products. For this purpose, the alcohol-insoluble residue (AIR) from several cultivars of apricots and peaches of different harvest seasons, provenances, and stages of ripeness was extracted and subsequently fractionated into acid- and EDTA/alkali-soluble pectins, hemicellulose, and cellulose. Each fraction was analysed for its neutral sugar composition by gas chromatography. In addition, analyses were also carried out on several cultivars of pumpkins because of their potential for use in fraudulent admixtures. Within the respective fruit species, characteristic neutral sugar profiles of the AIR and its fractions were observed, which were found to be independent of the cultivar, harvest season, and provenance. The fruit specific saccharide composition may be used for the differentiation of fruit products devoid of carbohydrate-based hydrocolloids. Furthermore, the isolated hemicellulose may also allow the detection of admixtures of non-specified fruit in complex fruit products, such as jams, spreads, and fruit preparations. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Apricot; Peach; Pumpkin; Authenticity; Cell wall composition; Monosaccharide composition; Fractional isolation

#### 1. Introduction

Apricots (*Prunus armeniaca* L.) and peaches (*Prunus persica* L.) are fruits of high economic relevance. Adulterations of apricot-based products with cheaper fruits or vegetables like peaches and pumpkins, resulting in deterioration of product quality, are difficult to detect. In order to protect the consumer as well to as avoid unfair competition it is absolutely essential to check the composition of a food at all levels of the production process, from the raw material to the finished product in terms of authenticity and quality. The various strategies for the detection of fraudulent admixtures to fruit products have recently been reviewed (Fügel, Carle, & Schieber, 2005; Reid, O'Donnell, & Downey, 2006). Numerous former studies focussed on the presence of characteristic phenolic compounds for the determination and differentiation of plant species (Alonso-Salces et al., 2004; Zimmermann & Galensa, 2007).

However, taking the phenolic composition as a parameter of food authenticity is not without problems and limitations. For example, the admixture of apricots to peach jam can easily be detected via the phenolic profile, whereas the detection of the more likely adulteration of the usually more expensive apricot jam by addition of peaches is impossible (García-Viguera, Ferreres, Tomás-Barberán, Gil, & Tomás-Lorente, 1992; Tomás-Lorente, García-Viguera, Ferreres, & Tomás-Barberán, 1992). Recent advances in food analytical chemistry, in particular the application of hyphenated techniques such as LC–MS and LC-NMR, have also demonstrated that some phenolic

<sup>\*</sup> Corresponding author. Tel.: +49 0 711 459 23125; fax: +49 0711 459 24110.

E-mail address: Schieber@uni-hohenheim.de (A. Schieber).

<sup>0308-8146/\$ -</sup> see front matter  $\odot$  2007 Elsevier Ltd. All rights reserved. doi:10.1016/j.foodchem.2007.05.078

compounds like phloridzin and isorhamnetin glycosides previously considered typical markers of apples and pears, respectively, may also be present in other genera (Hilt et al., 2003; Schieber, Keller, Streker, Klaiber, & Carle, 2002). Furthermore, several studies have shown that the phenolic composition undergoes qualitative and quantitative variations with different cultivars, stage of maturity, geographical origins and storage conditions (Lee, Kagan, Jaworski, & Brown, 1990; Lee, Park, & Choi, 2001; Senter, Robertson, & Meredith, 1989; Veberic & Stampar, 2005). In addition, owing to their susceptibility towards heat and oxygen, some polyphenolics may undergo degradation during industrial processing. Indisputable authentication of food products implies the need of highly sophisticated and cost-intensive analytical methods like NMR spectroscopy and IRMS (Pfammatter, Maury, & Théthaz, 2004; Schmidt, Roßmann, Stöckigt, & Christoph, 2005). DNAbased technologies using PCR technique are highly sensitive but inapplicable to heated, acidic products, since the DNA has been shown to degrade under these conditions (Adam & Zimm, 1977; Bauer, Weller, Hammes, & Hertel, 2003; Hupfer, Hotzel, Sachse, & Engel, 1998; Meyer, Rosa, Hischenhuber, & Meyer, 2001).

Studies on plant cell wall polysaccharides carried out so far aimed at their physiological function as a dietary fibre and their structure and organisation in fruits and vegetables. In terms of food quality, the main attention has been paid to cell wall changes during ripening in order to optimise textural attributes and cell wall-dependent quality characteristics (Waldron, Parker, & Smith, 2003). However, studies on the characterisation of the neutral sugar composition of the major cell wall constituents, pectin, hemicellulose, and cellulose, particularly with respect to authenticity control are scarce. Recently, an innovative approach has been reported for strawberries and cherries (Fügel, Carle, & Schieber, 2004). Therefore, the objective of the present study was to evaluate the possibility of differentiation of fruit species belonging to the same genus on the basis of the isolated cell wall components and their neutral sugar composition. Due to their economical significance, the main focus was on the investigation of apricots and peaches, both representing the genus Prunus. Pumpkins, which are likely candidates to be used for fraudulent purposes because of their carotene-based colour, were also included in this study.

# 2. Materials and methods

#### 2.1. Plant material

Fresh apricots (*Prunus armeniaca* L.) and peaches (*Prunus persica* L.) of different cultivars and provenances and yellow-fleshed pumpkins (*Cucurbita* sp.) were obtained from the local market (Stuttgart, Germany) (Table 1). IQF fruits (individually quick frozen after lye peeling (peaches) and blanching) were provided by Wild (Eppelheim/Heidelberg, Germany). Fresh apricots and peaches were

(lye) peeled and manually cored. An aliquot of selected fruit varieties remained unpeeled to determine the influence of (lye) peeling on cell wall polysaccharide composition. The pumpkins were manually peeled, cored, blanched at 85 °C for 10 min, and subsequently mashed through a sieve (mesh size: 1.5 mm). Fruits were harvested in 2003, 2004, 2005, and 2006. The fruits of 2003 and 2004 were stored, lyophilised in a Steris Lyovac<sup>®</sup> GT 4 Lyophilizer (Steris, Hürth, Germany) and frozen at -20 °C, respectively, to avoid enzymatic degradation of the cell wall material.

#### 2.2. Alcohol-insoluble residue (AIR)

Apricots, peaches, and pumpkin purées were freezedried and ground with liquid nitrogen to a fine powder in a cutter (Stephan und Söhne & Co., Hameln, Germany). The lyophilisate (25 g) was homogenised in boiling aqueous ethanol (300 mL, 80%, v/v) using an Ultra-Turrax blender. After boiling for 1 h, the insoluble solids were collected on a Büchner funnel. Ethanol extraction was repeated until a clear extract was obtained. The AIR was stirred overnight in pure acetone, passed through a G1 glass sinter filter and air-dried at 50 °C for 24 h. The dried AIR was ball-milled (Retsch, Haan, Germany), sealed in lever lid glass bottles and kept in a desiccator until further analysis.

#### 2.3. Sequential extraction of the AIR

The sequential extraction was based on a method described previously (Fügel, Förch, Carle, & Schieber, 2005) and optimised for apricots and peaches by an additional extraction step with hydrochloric acid. The AIR (800 mg) was suspended in 50 mL of diluted hydrochloric acid (0.05 M) and stirred at 60 °C for 1 h. After centrifugation at 15,000g for 20 min, the pellet was washed twice with 50 mL of distilled water. The supernatants were pooled, dialysed exhaustively against distilled water for 48 h using dialytic membranes (type 36/32, pore size 25–50 Å, Roth, Karlsruhe, Germany). Subsequently, the HCl-soluble pectin (HSP) fraction was freeze-dried. For further extraction of the residue, alkaline EDTA solution (0.05 NaOH; 0.5 mM EDTA) was used at 30 °C for 1.5 h. The suspension was centrifuged for 20 min at 15,000g and the remaining pellet washed twice with distilled water. The supernatants were pooled, adjusted to pH 6.5-7.0 with HCl, dialysed for 48 h against distilled water and freezedried to obtain the NaOH/EDTA-soluble pectin (OHEP) fraction. The final extraction was carried out using 50 mL of aqueous sodium hydroxide solution (16%, w/w) for 5 h at 30 °C. After centrifugation at 15,000g for 20 min, the pellet was rinsed twice with distilled water. The supernatants were pooled and adjusted to pH 6.5-7.0 with HCl, followed by the procedure described for the previous fraction to yield the hemicellulose (HC) fraction. The remaining pellet consisting of insoluble solids such as lignin and cellulose (C fraction) was suspended in 50 mL of distilled water, dialysed and lyophilised.

Table 1 Specification of fruit samples

Fruit species	Cultivar	Year of harvest	Ripening stage	Provenance	Sample code	
Apricot	Bergeron	2005	Ripe	France	A-B I	
•	Bergeron	2005	Ripe	France	A-B II	
	Bergeron	2006	Ripe	France	A-B III	
	Mixture <sup>a</sup>	2004	Ripe/turning	Unknown	A-M	
	Orange du Provence <sup>a</sup>	2005	Ripe	France	A-O	
	Orangered	2003	Unknown	Unknown	A-OR	
	Sekerpare	2005	Fully ripe	Turkey	A-S	
	Tyrinthe	2003	Unknown	Unknown	A-TR	
Peach	Elegant Lady	2005	Ripe/turning	Italy	P-EL	
	Flavor Crest	2005	Fully ripe	Spain	P-FC	
	Lara Star	2005	Ripe/turning	Italy	P-LS	
	Mixture <sup>a,b</sup>	2005	Ripe/turning	Greece	P-M	
	Maycrest	2003	Unknown	Spain	P-MR	
	Royal Glory	2005	Turning	Italy	P-RG	
	Spring Crest	2003	Unknown	Spain	P-SC	
	Unknown	2005	Ripe	Italy	P-U I	
	Unknown <sup>b</sup>	2006	Ripe/turning	Italy	P-U II	
Pumpkin	Golden Nuggets	2005	Ripe, yellow/orange	Germany	PK-GN	
*	Halloween	2005	Ripe, yellow	Germany	PK-HA	
	Hokkaido	2005	Ripe, orange	Germany	PK-HO	
	Muscade	2005	Ripe, orange	Germany	PK-MU	

<sup>a</sup> Blanched and individually quick frozen.

<sup>b</sup> Lye peeled.

#### 2.4. Hydrolysis of the cell wall fractions

Polysaccharide fractions and AIR were hydrolysed with sulphuric acid. For this purpose, 300  $\mu$ L of 2-propanol and 300  $\mu$ L of H<sub>2</sub>SO<sub>4</sub> (72%, w/w) were added to 20–30 mg of the AIR and the respective AIR fraction. After a reaction time of 1 h at room temperature, the suspension was diluted with 5 mL of distilled water and heated at 121 °C for 1 h. The hydrolysate was neutralised with 750  $\mu$ L of aqueous ammonia (25%, w/w). The volume was made up to 10 mL and an aliquot was centrifuged at 14,100*g* for 2 min. For the C fraction the volume of 2-propanol was decreased to 250  $\mu$ L, whereas sulphuric acid was increased to 500  $\mu$ L and 5.4 mL of distilled water were used for dilution. Additionally, cold hydrolysis was carried out in an ultrasonic bath for 2 h, and the hydrolysate was neutralised by addition of 1500  $\mu$ L of 25% aqueous ammonia (w/w).

#### 2.5. Analysis of neutral sugars by gas chromatography

The monosaccharides obtained after hydrolysis of the cell wall fractions were separated by gas chromatography with flame ionisation detection (GC-FID). For this purpose, the neutral sugars from an aliquot of the hydrolysed cell wall fractions were reduced with sodium borhydride and derivatised to their alditol acetates with acetic acid anhydride and 1-methylimidazole. For derivatisation, 1 mL of the hydrolysed sample, 100  $\mu$ L of the internal standard (2.0 g/L *myo*-inositol) and 100  $\mu$ L of ammonia (12 mol/L) were mixed. Subsequently, 100  $\mu$ L of freshly prepared sodium borhydride solution (750 mg NaBH<sub>4</sub>,

1.25 mL ammonia (12 mol/L) and 3.75 mL distilled water) was added. After 1 h at 40 °C, 100 µL of glacial acetic acid was pipetted and tempered at 20 °C. Aliquots of 500 µL were transferred in a glass tube and mixed with 500 mL of cold 1-methylimidazole and 5 mL of acetic acid anhydride. After 10 min at room temperature, 750 µL of absolute ethanol were added. After another 10 min, 5 mL of distilled water and 10 mL of potassium hydroxide solution (7.5 mol/L) were added. The upper layer was transferred to vials over anhydrous sodium sulphate and stored overnight at -20 °C until analysis. Aliquots of 1 µL were injected with a split ratio of 1:10. Helium was used as carrier gas at a flow rate of 37.94 cm/s. The GC (Chrompack CP 9001, Chrompack, Middleburg, NL) was fitted with a  $30 \text{ m} \times 0.25 \text{ mm}$  i.d., 0.15 µm fused silica capillary column (DB-225, J&W Scientific, Folsom, CA, USA) and equipped with a flame ionisation detector operated at 240 °C. The oven temperature was kept at 140 °C for 2 min, subsequently increased to 200 °C in 2 min and held isothermally for 4.5 min, followed by an increase to 220 °C in 1 min and final an isothermal hold at 220 °C for 18 min. Individual sugars were identified by comparison of their retention times with those of authentic standards of D(-)-ribose, D(+)-galactose, D(+)-glucose-monohydrate, D(+)-xylose, L(+)-arabinose, L(+)-rhamnose-monohydrate (Merck, Darmstadt, Germany), D(+)-mannose (Serva, Heidelberg, Germany), and L(-)-fucose (Sigma Chemical, St. Louis, MO, USA), and quantified using myo-inositol (Merck, Darmstadt, Germany) as an internal standard. Data analysis were carried out with the Maestro II 2.4 version software.

#### 2.6. Statistical analysis

In the case of significant differences, contents were compared using the Student's *t*-test (P < 0.05).

## 3. Results and discussion

# 3.1. Sequential extraction of the AIR

AIR isolation and fractionation of the fruits were carried out to determine the content of the cell wall components and the neutral sugar composition of the AIR and its fractions. Pectins were removed with hot diluted acid (HSP fraction) and cold alkaline EDTA solution (OHEP fraction). Hot hydrochloric acid solubilises protopectin by cleavage of glycosidic bonds. The chelating agent enhances solubilisation of unesterified pectins by complexing calcium and magnesium ions from their free carboxylic acid groups, while esterified pectic compounds and phenolic acids are hydrolysed by diluted alkali. Hemicelluloses are extracted with increasing alkali concentrations, whereas the remaining alkali-insoluble residue predominantly consists of cellulose.

The yellow coloured flesh of pumpkins which is due to the presence of carotenoids, may tempt unfair producers to adulterate apricot or peach product with pumpkin purée to improve the visual appearance and to feign a higher fruit content. Therefore, pumpkins were fractionated with the method developed for apricots and peaches. To standardise the extraction procedure, starch, which was present in pumpkins but absent in apricots and peaches was not removed.

The contents and composition of the AIR determined after extraction of fruit cell walls are shown in Table 2. In the manufacture of fruit products, apricots are generally processed without peeling, whereas peach products are mostly made from peeled fruits. Therefore, only selected peeled apricot samples and unpeeled peach samples were analysed. It can be seen that considerable differences were found for the amount of AIR from the different genera, ranging from 9.4% (apricot cv. Sekerpare, peeled) to 36.4% (pumpkin cv. Hokkaido). These differences were observed even within the individual apricot, peach, and pumpkin species, which may be attributed to different stages of maturity (Femenia, Sánchez, Simal, & Rosselló, 1998a). The AIR content of turning ripe mixed cultivars from apricots (A-M) and peaches (P-M) was significantly higher than from the fully ripe fruits, e.g. apricot cv. Sekerpare (A-S) and peach cv. Flavor Crest (P-FC). Expectedly, peeling decreased the AIR content of A-S by 46.3%, while differences in the AIR content of peeled and unpeeled peaches ranged between 4.3% (P-LS) and 20.9% (P-RG). The

Table 2

Amount and composition of the alcohol-insoluble residue (AIR) extracted from cell walls of apricots (A), peaches (P), and pumpkins (PK)

Sample <sup>c</sup>	AIR <sup>a</sup> (g/10	0 g DM)	Compositio	Recovery (%)								
			HSP		OHEP	OHEP			С			
	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled
Apricot												
A-B I		$15.4\pm0.6$		33.4		22.8		9.8		21.6		87.7
A-B II		$15.1\pm0.1$		31.8		23.8		10.8		21.2		87.6
A-B III	$17.4\pm0.2$		30.6		28.5		11.2		22.2		92.4	
A-M	$22.0\pm0.5$		31.2		24.2		10.5		20.6		86.5	
A-O	$17.8\pm0.2$		34.1		20.5		9.7		16.9		81.2	
A-OR	$17.1\pm0.2$		31.3		21.9		12.1		21.4		86.7	
A-S	$17.5\pm0.1$	$9.4\pm0.2$	32.3	22.3	26.2	34.3	12.2	11.5	20.1	18.5	90.8	86.5
A-TR	$21.5\pm0.2$		30.0		22.6		10.5		20.6		83.7	
Peach												
P-EL	$15.8\pm0.3$	$13.5\pm1.3$	25.9	25.7	29.1	31.9	13.8	12.4	14.5	16.2	83.2	86.3
P-FC		$16.4\pm0.4$		31.0		29.5		15.4		16.5		92.4
P-LS	$16.1\pm0.2$	$15.4 \pm 0.1$	25.5	24.5	29.5	36.2	13.0	13.0	16.1	17.7	84.2	91.3
P-M		$18.4\pm0.1$		32.7		31.6		11.8		13.0		89.1
P-MR		$18.9\pm0.3$		33.3		29.0		15.9		18.4		96.6
P-RG	$17.2\pm0.2$	$13.6 \pm 1.2$	30.2	27.1	30.1	32.9	12.9	13.1	16.4	17.0	89.6	90.0
P-SC		$17.0\pm0.1$		27.4		27.3		17.5		23.9		96.1
P-U I	$15.9\pm0.3$	$15.2 \pm 0.1$	32.6	28.2	31.1	30.2	13.3	12.2	15.0	16.0	92.0	86.6
P-U II		$14.5\pm0.1$		26.3		31.6		14.3		19.3		91.5
Pumpkin												
PK-GN		$27.8\pm0.02$		13.7		21.7		16.0		27.5		78.9
PK-HA		$29.2 \pm 1.1$		16.4		20.6		5.1		44.7		86.8
PK-HO		$36.4 \pm 1.1$		11.8		20.7		32.8		21.4		85.2
PK-MU		$18.3 \pm 0.7$		21.7		24.6		11.8		28.3		86.2

<sup>a</sup> Mean  $\pm$  SD of n = three replicate determinations.

<sup>b</sup> SD < 10%; *n* = three replicate determinations.

<sup>c</sup> For sample codes see Table 1.

difference did not correlate with fruit ripeness but depended on the size of the peeled fruits and their peel/flesh ratio (data not shown). In general, the AIR contents of the peaches were in the range of those reported by Chang and Smit (1974). The high AIR content of the pumpkins PK-GN, PK-HA and PK-HO may be attributed to co-extracted starch (de Escalda Pla et al., 2005), which was confirmed by the positive iodine-starch test, and may also alter the relative weights of the various groups of cell wall fractions (Selvendran, 1975).

The composition of the AIR of the stone fruits was dominated by the pectin fractions representing over 50% of the cell wall isolates. The high amounts of pectins, especially of acid-soluble pectins, are in agreement with the results published by Femenia, Sánchez, Simal, and Rosselló (1998b) and Souty, Thibault, Navarro-Garcia, Lopez-Roca, and Breuils (1981). While the pectin fractions are particularly affected by the degree of ripeness (Kunzek, Kabbert, & Gloyna, 1999), small changes were noted within the species. Within the pumpkins, amounts of pectic compounds were lower ranging from 32.4% to 46.3% of the AIR. Peeling decreased the acid soluble and increased the alkali/EDTA-soluble pectins of the fruits from the genus *Prunus*. These findings indicate different compositions of the pectic substances within the mesocarp and the peel of the fruits. In contrast to the HSP and OHEP fractions, the HC fraction was inconsiderably affected by peeling. In accordance with a former study on strawberries and cherries (Fügel et al., 2004), the content of the HC and C fraction proved to be rather constant within different *Prunus* species except for the amounts of the peach variety Spring Crest (P-SC), showing slightly higher hemicellulose and cellulose proportion.

The composition of the AIR from the diverse pumpkin varieties differed considerably, which might be due to their different starch content and a more heterogeneous composition of the cell wall material within the *Cucurbita* species. The high cellulose contents of the pumpkins ranging from 21.4% to 44.7% are in accordance with a previous study (Ratnayake, Melton, & Hurst, 2003).

# 3.2. Monosaccharide composition of AIR and AIR fractions

The neutral saccharide composition of the AIR from apricots and peaches was dominated by arabinose and galactose (Table 3). The arabinose content ranged from 36.7% to 47.3% in apricots and 41.9% to 48.2% in peaches. Galactose contents in apricots were 19.6-22.8% and 22.6-26.4% in peaches respectively. This result is not surprising, taking into account that these are typical sugars

Table 3

Neutral sugar composition of the AIR from the cell walls of apricots (A), peaches (P), and pumpkins (PK)

	Rhamnos	e	Fucose		Ribose		Arabinose		Xylose		Mannose		Galactose		Glucose	
	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeleo
Apricot																
4-B I		5.5		2.0		nd <sup>a</sup>		42.4		16.2		4.8		19.6		9.4
A-B II		6.5		2.3		nd		40.5		15.6		4.8		21.3		9.0
A-B III	5.3		2.0		nd		43.5		16.0		4.8		19.7		8.7	
A-M	6.5		2.3		nd		40.2		14.1		5.6		21.9		9.5	
<b>A-O</b>	6.5		2.2		nd		44.5		12.0		4.7		21.1		9.0	
A-OR	5.5		2.2		nd		37.3		15.5		6.0		20.2		13.3	
A-S	4.2	7.1	2.3	3.0	nd	nd	41.5	47.3	14.6	11.8	4.8	2.9	20.8	22.8	8.8	8.1
A-TR	6.6		2.4		tr <sup>b</sup>		36.7		14.3		5.4		22.7		12.0	
Peach																
P-EL	4.2	3.8	2.7	2.7	nd	nd	45.9	46.6	10.9	9.6	2.9	2.6	25.4	27.1	8.1	7.6
P-FC		4.5		3.3		tr		43.9		12.0		3.1		24.1		8.8
P-LS	4.3	3.9	3.4	3.3	tr	tr	44.6	44.7	12.4	13.0	2.7	2.8	24.4	24.2	8.1	8.1
P-M		3.9		2.7		tr		47.8		11.1		2.3		25.5		6.4
P-MR		3.3		2.2		nd		43.4		14.5		3.4		25.9		7.4
P-RG	4.4	4.5	3.1	3.2	tr	nd	47.7	48.2	11.4	11.0	2.9	2.7	22.6	22.6	7.8	7.8
P-SC		3.8		2.3		nd		41.9		13.9		3.5		26.2		8.3
P-U I	4.3	4.5	3.0	3.1	nd	nd	46.9	46.8	10.9	10.9	2.9	2.7	25.7	25.1	6.3	7.1
P-U II		4.5		3.1		nd		43.8		12.5		3.1		24.3		8.8
Pumpkin																
PK-GN		3.3		0.6		tr		7.1		5.9		3.5		14.7		64.5
PK-HA		9.7		2.2		nd		7.6		16.2		10.0		13.5		40.8
РК-НО		1.3		tr		tr		3.6		2.5		2.1		9.2		80.8
PK-MU		5.3		1.1		nd		8.4		8.7		5.3		13.6		57.5

<sup>a</sup> Not detectable.

<sup>b</sup> Traces: <0.5%.

 $^{\rm c}$  Results were obtained from duplicates, SD  ${<}10\%$ 

<sup>d</sup> For sample codes see Table 1.

originating from *Prunus* pectic material (Brummell, Dal Cin, Crisosto, & Labavich, 2004; Hegde & Maness, 1996, 1998; Muramatsu, Tanaka, Asakura, & Haji, 2004) and, as mentioned before, more than 50% of the AIR consists of pectins. Furthermore, since cellulose hydrolysis occurs only under conditions harsher than those applied for the saccharide analysis of the AIR, glucose does not play an important role. In contrast, high glucose contents of the pumpkin species resulted from starch hydrolysis.

Whereas the AIR of the stone fruits showed comparable neutral sugar distributions, remarkable differences to the sugar profiles of the pumpkins were observed (Table 3). Glucose was the predominant monosaccharide in all pumpkin varieties investigated. However, in contrast to peaches and apricots, pronounced differences in the sugar contents were found for the pumpkins. These findings are in agreement with the results of a previous study (Gross & Sams, 1984). Within the pumpkin varieties striking differences of the sugar profiles occurred. Especially the rhamnose, mannose and glucose amounts differed remarkably within the *Cucurbita* species.

Consistent with the findings reported by Chapman and Horvat (1990), Femenia et al. (1998a) and Brummell et al. (2004), in the pectin containing fractions HSP and OHEP (Tables 4 and 5) of the stone fruits, arabinose and galactose were the principal neutral sugars. Xylose, glucose, ribose, and fucose were minor constituents. The neutral sugar ratios of the stone fruits did not differ except for rhamnose, which was present in lower quantities in peaches. Although arabinose, galactose and rhamnose were also major saccharides in pumpkin pectins, significant differences were found in the amounts of the sugars compared to those in the HSP and OHEP fractions of apricots and peaches. Furthermore, the sugar composition in the pectin fractions of the pumpkins was less uniform compared to the profiles of the stone fruits, which may be attributed to their different cell wall material and starch contents (Corrigan, Hurst, & Potter, 2001). According to Irving, Shingleton, and Hurst (1999), they may be affected by degree of ripening and period of storage.

The main neutral sugar of the HC fraction of the stone fruits was glucose, followed by xylose and galactose (Table 6). The amounts of these saccharides were almost identical. Furthermore, peeling did not affect the neutral sugar profiles of the stone fruits. Astonishingly, significant differences between peaches and apricots were observed in the arabinose and mannose content, thus allowing differentiation of the *Prunus* species. Fucose, a characteristic constituent of xyloglucans (Fry, 1989), was a typical neutral sugar of this fraction. Ribose was not detectable. The neutral

Table 4

Neutral sugar composition of the HSP fractions from the cell walls of apricots (A), peaches (P), and pumpkins (PK)

	Rhamnos	e	Fucose		Ribose	Ribose			Xylose		Mannose		Galactose		Glucose	
	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled
Apricot																
A-B I		9.9		tr <sup>b</sup>		nd <sup>a</sup>		64.1		2.4		0.7		19.1		3.3
A-B II		11.4		tr		nd		60.3		2.9		0.6		21.3		3.1
A-B III	7.4		0.5		nd		65.9		2.2		1.4		19.2		3.4	
A-M	10.7		tr		nd		61.5		2.2		1.3		20.3		3.5	
A-O	10.7		tr		nd		64.0		2.4		0.7		18.6		3.2	
A-OR	10.9		1.0		0.8		57.0		2.7		1.9		21.8		3.8	
A-S	11.3	10.8	0.5	tr	nd	nd	60.3	60.6	3.2	3.2	0.6	0.8	20.6	20.9	3.5	3.3
A-TR	10.6		0.5		nd		57.0		2.7		1.8		22.6		4.9	
Peach																
P-EL	5.1	4.3	0.7	0.7	nd	nd	53.9	54.2	3.6	3.3	0.6	0.7	31.1	32.1	5.0	4.7
P-FC		6.3		0.8		nd		51.3		3.6		0.8		31.5		5.8
P-LS	4.8	4.3	0.5	0.5	nd	nd	51.0	53.1	2.8	3.1	0.8	0.8	36.3	34.4	3.8	3.8
P-M		4.9		0.6		nd		58.6		3.3		0.6		27.2		4.9
P-MR		5.7		0.8		tr		52.3		5.1		1.7		30.4		3.7
P-RG	5.2	4.6	0.5	0.6	nd	nd	56.4	55.2	2.5	3.0	0.7	0.8	31.0	31.3	3.7	4.6
P-SC		5.5		0.9		0.5		53.8		2.8		1.8		29.8		4.9
P-U I	4.2	5.7	0.6	0.7	nd	nd	53.8	56.1	3.2	2.8	0.8	0.6	32.9	29.4	4.3	4.6
P-U II		4.4		1.0		tr		52.4		4.0		1.2		31.0		6.0
Pumpkin																
PK-GN		5.3		nd		nd		15.3		tr		2.7		23.7		52.8
PK-HA		16.8		tr		nd		27.5		0.8		9.6		31.8		13.1
PK-HO		4.3		nd		nd		10.9		tr		3.4		18.4		62.8
PK-MU		8.2		tr		nd		20.2		2.0		2.7		23.8		43.0

<sup>a</sup> Not detectable.

 $^{\rm b}$  Traces: <0.5%.

 $^{\rm c}\,$  Results were obtained from duplicates, SD < 10%.

<sup>d</sup> For sample codes see Table 1.

sugar profiles of the hemicellulose were even different from those of cherries, also belonging to the genus *Prunus* (*P. cerasus* L.), which were investigated in a former study (Fügel et al., 2004). The xylose content of the cherries was considerable lower than the contents of the *Prunus* species determined in the present study.

The proportion of saccharides in the HC varied within different *Cucurbita* cultivars. Glucose and xylose were the major neutral monosaccharides, with glucose partially originating from starch. The pumpkin HC fraction was also characterised by virtually negligible amounts of mannose.

As expected, glucose was the predominant compound in the insoluble residue (C fraction), ranging from 66.7% to 80.7% of total sugars in the insoluble residue of the stone fruits and 86.4–90.4% in the pumpkins. This great divergence might be attributed to both incomplete hydrolysis of cellulose by sulphuric acid and residual starch. Small amounts of the typical pectic saccharides such as galactose, arabinose and xylose, mannose and traces of fucose originating from hemicellulose indicate their incomplete removal during sequential fractionation. This is also confirmed by the detection of small amounts of rhamnose originating from rhamnogalacturonans incorporated in residual pectic material, which could not be removed even by extended extraction with sodium hydroxide solution (data not shown).

From the neutral sugar profiles obtained by characterisation of the AIR, pectins, hemicellulose, and cellulose fractions, characteristic fruit specific patters were obtained which could serve as fingerprints. The alcohol-insoluble residue as well as pectic fractions (HSP and OHEP) could serve for fruit differentiation of fruit purées, which do not contain hydrocolloids. For example, fraudulent admixtures of pumpkins to apricot or peach purée would result in a decrease of the arabinose content and an increase of the glucose content within the sugar composition of the stone fruits (Tables 3–5). In contrast, admixtures of peach purée to apricot cannot be detected by means of the neutral sugar profiles of the pectin fractions because of their very similar neutral sugar profiles.

For more complex products like jams, spreads and fruit preparations, containing a multitude of ingredients such as sugars, colouring foodstuffs, thickening agents, flavours, essences and consumable acids, the detection of adulterations usually proves difficult. While hydrocolloids are also precipitated during preparation of the AIR and solubilised by acid and alkaline/EDTA solution, the AIR and the

Table 5

Neutral sugar composition of the OHEP fractions from the cell walls of apricots (A), peaches (P), and pumpkins (PK)

Sumple	Composition of ne												<u>a</u> 1 .			
	Rhamnos	•	Fucose		Ribose		Arabinose	•	Xylose		Mannose		Galactose		Glucose	
	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeleo
Apricot																
A-B I		10.3		tr <sup>b</sup>		1.9		67.2		4.2		nd <sup>a</sup>		14.9		1.4
A-B II		14.7		tr		1.6		63.2		4.4		nd		14.3		1.6
A-B III	10.1		tr		1.6		70.4		2.8		tr		13.0		1.4	
A-M	12.7		tr		1.6		63.8		3.3		nd		17.5		1.0	
A-O	12.0		tr		1.2		64.8		4.5		nd		15.8		1.4	
A-OR	14.0		0.8		2.5		62.1		4.0		0.6		14.0		1.9	
A-S	11.0	12.8	tr	tr	1.5	1.5	66.3	64.9	5.1	4.9	nd	nd	14.1	14.2	1.8	1.6
A-TR	14.6		tr		1.4		60.8		4.2		nd		17.5		1.2	
Peach																
P-EL	7.5	7.9	tr	tr	1.0	1.0	66.6	61.8	2.6	2.2	nd	nd	21.1	25.9	1.1	1.1
P-FC		10.8		tr		1.9		63.8		3.2		nd		18.5		1.8
P-LS	8.8	9.3	tr	tr	1.9	2.2	66.3	64.3	3.0	2.9	nd	tr	17.9	19.3	1.8	1.8
P-M		7.5		tr		1.6		60.2		3.5		nd		25.2		1.8
P-MR		7.1		0.6		2.0		56.4		7.5		1.4		23.4		1.6
P-RG	9.3	8.3	tr	tr	1.4	1.6	69.9	69.8	2.6	2.6	nd	nd	15.1	15.9	1.6	1.6
P-SC		8.4		0.7		2.5		54.7		3.4		0.7		27.9		1.7
P-U I	8.5	9.0	tr	tr	1.3	1.2	62.5	62.6	2.5	2.6	nd	tr	23.6	22.6	1.4	1.6
P-U II		6.0		tr		2.1		73.6		2.3		tr		14.3		1.0
Pumpkin																
PK-GN		5.2		nd		4.0		14.5		0.9		tr		27.0		48.2
PK-HA		24.7		tr		8.0		28.5		2.5		0.5		33.0		2.5
PK-HO		3.3		nd		4.5		9.6		tr		tr		22.1		60.0
PK-MU		14.7		tr		2.5		20.6		4.6		0.8		31.4		25.2

<sup>a</sup> Not detectable.

<sup>b</sup> Traces: <0.5%.

 $^{\rm c}$  Results were obtained from duplicates, SD  $\leq$  10%.

<sup>d</sup> For sample codes see Table 1.

Neutral sugar composition of the HC fractions from the cell walls of apricots (A), peaches (P), and pumpkins (PK)

Sample <sup>d</sup>	Composition of neutral sugars (relative mass%) <sup>c</sup>													
	Rhamnose	;	Fucose		Arabinose		Xylose		Mannose		Galactose		Glucose	
	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled	Unpeeled	Peeled
Apricot														
A-B I		1.0		3.2		4.6		25.7		11.2		17.7		36.5
A-B II		1.0		3.0		5.6		26.9		10.1		16.7		36.6
A-B III	1.2		3.2		7.2		27.8		12.2		17.0		31.5	
A-M	1.1		3.2		5.0		23.2		11.8		19.2		36.5	
A-0	1.3		3.2		4.1		23.8		11.8		19.3		36.4	
A-OR	1.3		3.4		5.6		25.8		11.3		18.1		34.4	
A-S	1.8	1.0	3.3	3.1	6.4	6.7	26.8	25.9	9.8	10.2	17.9	16.9	34.0	36.1
A-TR	0.9		3.6		4.3		22.4		11.3		19.2		38.3	
Peach														
P-EL	1.2	1.2	4.4	4.4	16.1	15.8	24.2	22.2	4.6	4.5	16.5	17.5	33.0	34.4
P-FC		1.3		5.1		12.7		23.2		4.0		16.2		37.6
P-LS	1.2	1.5	5.1	4.3	14.3	16.6	23.7	23.3	4.5	3.9	15.8	14.8	35.4	35.4
P-M		0.9		4.4		12.5		25.0		5.0		16.4		35.7
P-MR		1.0		4.2		13.2		24.9		6.7		17.1		32.8
P-RG	1.3	1.3	4.4	4.8	12.5	14.4	23.5	23.2	4.8	4.2	15.3	15.3	35.6	36.7
P-SC		1.1		4.2		11.4		27.7		6.5		16.3		32.7
P-U I	1.2	1.2	4.4	4.5	15.2	14.8	24.1	23.7	4.6	4.6	16.3	16.0	34.3	35.2
P-U II		1.2		4.8		17.3		24.5		5.2		15.9		31.0
Pumpkin														
PK-GN		0.8		nd <sup>a</sup>		3.7		6.2		tr <sup>b</sup>		9.1		79.9
PK-HA		5.0		2.8		4.8		44.2		1.0		12.2		30.0
PK-HO		tr		nd		1.6		2.0		tr		6.5		89.3
PK-MU		2.6		0.6		3.7		20.1		0.5		8.0		64.4

<sup>a</sup> Not detectable.

<sup>b</sup> Traces: <0.5%.

<sup>c</sup> Results were obtained from duplicates, SD < 10%.

<sup>d</sup> For sample codes see Table 1.

pectin fractions are unsuitable for the detection of fraudulent admixtures in hydrocolloid containing products. Due to acidic hydrolysis of the hydrocolloids, monosaccharides derived therefrom would change the authentic sugar profiles of the fruits.

In a previous study it has been shown for the first time that the neutral sugar profile of the HC from strawberries and cherries can be used as a fingerprint (Fügel et al., 2004). The outcome of the present investigation supported the fruit specific saccharide profiles of the HC fraction for apricots and peaches. Contrary to the pectin fractions, the hemicellulose has been found to be particularly suitable for the identification of fruit species in complex matrices like fruit preparations. The hydrocolloids added to these products are extracted with the pectins originating from the fruit in the preliminary extraction steps with diluted acid and diluted alkali and EDTA solution. From Table 6 it becomes evident that the genuine profile of monosaccharides from this fraction differed, so that they can serve as a fruit specific fingerprint. Since (lye) peeling did not affect the neutral sugar profiles of the HC fraction, the knowledge of fruit pre-treatment is not required. For instance, high mannose and low arabinose contents of apricots compared to low mannose and higher arabinose contents in peaches allow the differentiation of fruits even from the

same genus. The adulteration of peach and apricots with pumpkin mash could easily be detected by an increase of the glucose content and a decrease in galactose, fucose and mannose (except cv. Halloween). The admixture of the Halloween pumpkin would lead to an increase of the xylose and of the rhamnose content. Especially the ratios of the sugars galactose, glucose, and xylose to mannose in the HC fractions showed fruit specific differences. The ratios in the HC of the peaches were twice as much as the corresponding ratios in the fraction of the apricots. The relative amounts found in the different pumpkins differed even about 3-96 times compared to the corresponding sugar ratios in apricots and peaches. According to these results, fraudulent admixtures of peach and pumpkin to apricot, or pumpkin to peach, would obviously alter the fruit specific relative amounts of galactose, glucose, and xylose to mannose.

The hemicellulose fraction is also of particular interest for the quality control of fruit products, principally the determination of their fruit content. Methods described so far are mostly based on the quantification of low molecular compounds such as pigments, amino and organic acids as well as minerals (Fügel, Carle, et al., 2005). However, these compounds are added to the products e.g. as colouring foodstuff and consumable acids and can easily be manipulated in order to feign higher fruit content. As a consequence, methods based on low molecular constituents are not reliable for the determination of the fruit content of complex products.

In former studies hemicellulose as a high molecular compound of the cell wall material has been found suitable for the fruit content determination of fruit preparations and yoghurt (Fügel, Schieber, & Carle, 2005; Fügel, Förch, et al., 2005; Schieber, Fügel, Henke, & Carle, 2005). Hemicellulose is not degraded through processing and much less susceptible to adulterations and can easily be isolated from food ingredients usually added to fruit preparations, spreads, and jams, and determined gravimetrically. According to Hegde and Maness (1996), the hemicellulose content within the stone fruit species varied only little, and neither cultivar nor provenance and stage of ripeness affected its content (Table 2). The process stability of hemicellulose was also confirmed by Coimbra, Waldron, Delgadillo, and Selvendran (1996) and Reinders and Thier (1999). According to the present study, (lye) peeling did not affect the amount of hemicellulose, which has shown remarkable constancy, thus providing a reliable basis for the determination of fruit contents, even in complex recipes.

#### 4. Conclusions

This investigation clearly demonstrated that the sequential fractionation of the AIR and subsequent determination of the neutral sugar composition may serve as a valuable tool for authenticity control of apricot and peach products devoid of hydrocolloids. Furthermore, this study shows for the first time that the neutral sugar composition of the isolated hemicelluloses and the ratio of the sugars allow the differentiation of fruit species even from the same genus (P. armeniaca L. and P. persica L.). However, it should be noted that only a limited number of samples could be investigated, which may of course lead to limitations of the method in general. Data of further varieties will be compiled in order to obtain a more comprehensive database and to better estimate these limitations. The method applied is less tedious and time-consuming than that published in a former study and was developed to efficiently isolate the hemicellulose fraction from apricots and peaches, which has been shown to be a valuable tool for fruit content determination. The determination of the fruit content of apricot jams and spreads as well as peach and apricot fruit preparations is a matter of our current studies and will be presented in a forthcoming communication.

# Acknowledgements

The present work was supported by the Research Association of the German Food Industry (FEI), the German Federation of Industrial Research Associations (AiF) and the Federal Ministry of Economics and Labour (BMWi). The authors want to thank Ms. K. Meisberger for her excellent technical assistance.

#### References

- Adam, R., & Zimm, B. (1977). Shear degradation of DNA. Nucleic Acid Research, 4, 1513–1537.
- Alonso-Salces, R. M., Ndjoko, K., Queiroz, E. F., Ioset, J. R., Hostettmann, K., Berrueta, L. A., et al. (2004). On-line characterisation of apple polyphenols by liquid chromatography coupled with mass spectrometry and ultraviolet absorbance detection. *Journal of Chromatography A*, 1046, 89–100.
- Bauer, T., Weller, P., Hammes, W. P., & Hertel, C. (2003). The effect of processing parameters on DNA degradation in food. *European Food Research and Technology*, 217, 338–343.
- Brummell, D. A., Dal Cin, V., Crisosto, C. H., & Labavich, J. M. (2004). Cell wall metabolism during maturation, ripening and senescence of peach fruit. *Journal of Experimental Botany*, 55, 2029–2039.
- Chang, Y. S., & Smit, C. J. B. (1974). Characteristics of pectins isolated from soft and firm fleshed peach varieties. *Journal of Food Science*, 38, 646–648.
- Chapman, G. W., Jr., & Horvat, R. J. (1990). Changes in nonvolatile acids, sugars, pectin, and sugar composition of pectin during peach (cv. Monroe) maturation. *Journal of Agricultural and Food Chemistry*, 38, 383–387.
- Coimbra, M. A., Waldron, K. W., Delgadillo, I., & Selvendran, R. R. (1996). Effect of processing on cell wall polysaccharides of green table olives. *Journal of Agricultural and Food Chemistry*, 44, 2394–2401.
- Corrigan, V. K., Hurst, P. L., & Potter, J. F. (2001). Winter squash (*Cucurbita maxima*) texture: Sensory, chemical, and physical measures. New Zealand Journal of Crop and Horticultural Science, 29, 111–124.
- De Escalda Pla, M. F., Ponce, N. M., Wider, M. E., Stortz, C. A., Rojas, A. M., & Gerschenson, L. N. (2005). Chemical and biochemical changes of pumpkin (*Cucumis moschata*, Duch) tissue in relation to osmotic stress. *Journal of the Science of Food and Agriculture*, 85, 1852–1860.
- Femenia, A., Sánchez, E. S., Simal, S., & Rosselló, C. (1998a). Developmental and ripening-related effects on the cell wall of apricot (*Prunus armeniaca*) fruit. Journal of the Science of Food and Agriculture, 77, 487–493.
- Femenia, A., Sánchez, E. S., Simal, S., & Rosselló, C. (1998b). Modification of cell wall composition of apricots (*Prunus armeniaca*) during drying and storage under modified atmospheres. *Journal of Agricultural and Food Chemistry*, 46, 5248–5253.
- Fügel, R., Carle, R., & Schieber, A. (2004). A novel approach to quality and authenticity control of fruit products using fractionation and characterization of cell wall polysaccharides. *Food Chemistry*, 87, 141–150.
- Fügel, R., Schieber, A., & Carle, R. (2005). Determination of the fruit content of cherry fruit preparations by gravimetric quantification of hemicellulose. *Food Chemistry*, 95, 163–168.
- Fügel, R., Förch, M., Carle, R., & Schieber, A. (2005). Determination of the fruit content of strawberry yoghurt by gravimetric quantification of hemicellulose. *Journal of Applied Botany and Food Quality*, 79, 157–159.
- Fügel, R., Carle, R., & Schieber, A. (2005). Quality and authenticity control of fruit purées, fruit preparations and jams – a review. *Trends* in Food Science & Technology, 16, 433–441.
- Fry, S. C. (1989). The structure and functions of xyloglucan. Journal of Experimental Botany, 40, 1–11.
- García-Viguera, C., Ferreres, F., Tomás-Barberán, F. A., Gil, M. I., & Tomás-Lorente, F. (1992). Detection of adulterations in fruit jams by HPLC/diode array analysis of flavonoids. *Bulletin de Liasison-Groupe Polyphenols, 16*, 362–366.
- Gross, K. C., & Sams, C. E. (1984). Changes in cell wall neutral sugar composition during fruit ripening: A species survey. *Phytochemistry*, 23, 2457–2461.

- Hegde, S., & Maness, N. O. (1996). Sugar composition of pectin and hemicellulose extracts of peach fruit during softening over two harvest seasons. *Journal of the American Society of Horticultural Science*, 121, 1162–1167.
- Hegde, S., & Maness, N. O. (1998). Changes in apparent molecular mass of pectin and hemicellulose extracts during peach softening. *Journal of* the American Society of Horticultural Science, 123, 445–456.
- Hilt, P., Schieber, A., Yildirim, C., Arnold, G., Conrad, J., Klaiber, I., et al. (2003). Detection of phloridzin in strawberries (*Fragaria×anan-assa* Duch.) by HPLC-PDA-MS/MS and NMR spectroscopy. *Journal of Agricultural and Food Chemistry*, 51, 2896–2899.
- Hupfer, C., Hotzel, H., Sachse, K., & Engel, K.-H. (1998). Detection of genetic modification in heat-treated products of Bt maize by polymerase chain reaction. *Zeitschrift für Lebensmittel-Untersuchung* und Forschung, 206, 203–207.
- Irving, D. E., Shingleton, G. J., & Hurst, P. L. (1999). Starch degradation in buttercup squash (*Cucurbita maxima*). Journal of the American Society for Horticultural Science, 124, 587–590.
- Kunzek, H., Kabbert, R., & Gloyna, D. (1999). Aspects of material science in food processing: Changes in plant cell walls of fruits and vegetables. *Zeitschrift für Lebensmittel-Untersuchung und Forschung* A: Food Research and Technology, 208, 233–250.
- Lee, C. Y., Kagan, V., Jaworski, A. W., & Brown, S. K. (1990). Enzymatic browning in relation to phenolic compounds and polyphenoloxidase activity among various peach cultivars. *Journal of Agricultural and Food Chemistry*, 38, 99–101.
- Lee, J.-Y., Park, H.-D., & Choi, S.-W. (2001). Physiochemical characteristics of various peach cultivars. *Journal of Food Science and Nutrition*, 6, 107–111.
- Meyer, K., Rosa, C., Hischenhuber, C., & Meyer, R. (2001). Determination of locust bean gum and guar gum by polymerase chain reaction and restriction fragment length polymorphism analysis. *Journal of* AOAC International, 84, 89–99.
- Muramatsu, N., Tanaka, K., Asakura, T., & Haji, T. (2004). Changes in cell wall polysaccharides and physical properties of peach (*Prunus persica* Batsch) fruit during ripening. *Journal of the Japanese Society* for Horticultural Science, 73, 534–540.
- Pfammatter, E., Maury, V., & Théthaz, C. (2004). Nachweis der Authentizität von Lebensmitteln mittels IRMS (Isotope ratio Mass Spectrometry) und Anwendung dieser Methodik im Bereich der Lebensmittelkontrolle. *Mitteilungen aus Lebensmitteluntersuchung und Hygiene*, 95, 585–596.

- Ratnayake, R. M. S., Melton, L. D., & Hurst, P. L. (2003). Influence of cultivar, cooking, and storage on cell-wall polysaccharide composition of winter squash (*Cucurbita maxima*). Journal of Agricultural and Food Chemistry, 51, 1904–1913.
- Reid, L. M., O'Donnell, C. P., & Downey, G. (2006). Recent technological advances for the determination of food authenticity. *Trends in Food Science & Technology*, 17, 344–353.
- Reinders, G., & Thier, H.-P. (1999). Non-starch polysaccharides of tomatoes. II. Influence of thermal processing. *European Food Research* and Technology, 209, 47–51.
- Selvendran, R. R. (1975). Analysis of cell wall material from plant tissues: Extraction and purification. *Phytochemistry*, 14, 1011–1017.
- Senter, S. D., Robertson, J. A., & Meredith, F. I. (1989). Phenolic compounds of the mesocarp of cresthaven peaches during storage and ripening. *Journal of Food Science*, 54, 1259–1268.
- Schieber, A., Keller, P., Streker, P., Klaiber, I., & Carle, R. (2002). Detection of isorhamnetin glycosides in extracts of apples (*Malus domestica* cv. Brettacher) by HPLC-PDA and HPLC-APCI-MS/MS. *Phytochemical Analysis*, 13, 87–94.
- Schieber, A., Fügel, R., Henke, M., & Carle, R. (2005). Determination of the fruit content of strawberry fruit preparations by gravimetric quantification of hemicellulose. *Food Chemistry*, 91, 365–371.
- Schmidt, H.-L., Roßmann, A., Stöckigt, D., & Christoph, N. (2005). Stabilisotopenanalytik. Herkunft und Authentizität von Lebensmitteln. *Chemie in Unserer Zeit*, 39, 90–99.
- Souty, M., Thibault, J.-F., Navarro-Garcia, G., Lopez-Roca, J.-M., & Breuils, L. (1981). The pectic substances from apricot (*Prunus armeniaca* L.) c.v. Rouge du Roussillon. General characteristics and ion exchange chromatography study. *Sciences des Aliments*, 1, 67–80.
- Tomás-Lorente, F., García-Viguera, C., Ferreres, F., & Tomás-Barberán, F. A. (1992). Phenolic compounds analysis in the determination of fruit jam genuineness. *Journal of Agricultural and Food Chemistry*, 40, 1800–1804.
- Veberic, R., & Stampar, F. (2005). Selected polyphenols in fruits of different cultivars of genus *Prunus*. *Phyton*, 45, 375–383.
- Waldron, K. W., Parker, M. L., & Smith, A. C. (2003). Plant cell walls and food quality. *Comprehensive Reviews in Food Science and Food Safety*, 2, 101–119.
- Zimmermann, B. F., & Galensa, R. (2007). One for all-all for one: Proof of authenticity and tracing of foods with flavonoids. *European Food Research and Technology*, 224, 385–393.